



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
REGION III  
841 Chestnut Building  
Philadelphia, Pennsylvania 19107-4431

133434

Hazardous Waste Management Division  
Office of Superfund  
Pennsylvania Remedial Branch  
Western Pennsylvania Section

Dave Turner, Remedial Project Manager  
Mail Code (3HW23)  
Direct Dial (215) 597-3218  
FAX (215) 597-9890

via Federal Express 1017176414

Ms. Ruth Bishop  
Commonwealth of Pennsylvania  
Department of Environmental Resources  
Bureau of Waste Management  
One Ararat Boulevard  
Harrisburg, PA 17110

July 1, 1994

RE: York County Solid Waste Landfill Superfund Site  
Revised Draft Feasibility Study (FS)  
EPA's Review Comments

Dear Ms. Bishop:

As discussed during our June 24, 1994 tele-conference the U. S. Environmental Protection Agency (EPA) has preformed its review of the document: Revised DRAFT Feasibility Study (FS) Report York County Solid Waste Landfill (Site) May 1994, submitted by the York County Solid Waste and Refuse Authority (YCSWRA).

The enclosed, and the comments previous sent on May 31, 1994, represent all of EPA's FS comments except for the comments from the NEPA (National Environmental Policy Act) coordinator. The NEPA coordinator's comments were not available at the time of this mailing. NEPA comments will be forthcoming in the next week, and I will send them to you as soon as they are received.

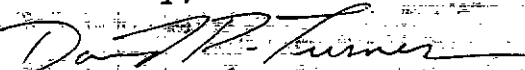
The EPA comments must be addressed by the YCSWRA prior to the finalization of the FS. YCSWRA's responses should occur during the public comment period of the Proposed Plan, with all

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YCSWRA responses submitted by the end of the comment period. This will allow enough time for reviewing YCSWRA responses for adequacy, drafting the Record of Decision (ROD) and Responsiveness Summary documents. The EPA accepts the FS as final when comments are addressed adequately and the Site ROD is signed by the EPA Region III Regional Administrator.

If you have any questions, please do not hesitate to contact me.

Sincerely,

  
David P. Turner  
RPM, Environmental Engineer

Enclosure

cc: Pike (3HW23) Davis (3HW15) Flores (3AT11)  
Hubbard (3HW15) Burr FWS (3HW15)  
Kargbo (3HW13) Gross (3WM41)  
Nishitani (3RC31) Donor (3HW23)  
Vollero, YCSWRA w/ Attachment

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A. EPA Water management Division, Drinking Water Section  
Comments:

- 1) pg. 1-20 How long will the two residents receiving bottled water continued being supplied potable water if the contaminants are not site related? This was not mentioned in the FS. And if this service is to be discontinued, how are we planning eliminate this risk to the residents?

- 2) TABLE 2-5 Please revise.

Silver does not have an MCL of 50  $\mu\text{g/l}$ . Silver has an Secondary Maximum Contaminant Level (SMCL) of 100  $\mu\text{g/l}$ . A SMCL is a number associated with the aesthetic quality of the water such as odor, or color. Water with contaminants above the SMCL may not be pleasant to drink, but it will not cause health problems.

Methylene chloride does not have an MCL under the Safe Drinking Water Act.

- 3) pg 2-10 section 2.5.2.2 Point of Entry Treatment.  
Are the carbon filtration units currently supplied by the Authority to eight residents with contaminated wells to be supplied indefinitely? If so, this is not thought to be a permanent remedy for contaminated drinking water supplies and not fully protective of human health.

B. Air/Superfund Comments:

Question 1 - The PRPs include estimations of air concentrations using the SCREEN model, based on groundwater concentrations and the properties of the air strippers (Tables 4-9 and 4-10). It is crucial to the risk evaluation to know whether these concentrations were appropriately calculated.

According to the Feasibility Study, the emission rates of organic vapors from the air stripper exhaust were determined based on ground-water chemical concentrations from the Remedial Investigation sampling, assuming an air stripper removal efficiency of 100% and no air pollution controls. These emission rates were used in the EPA air dispersion model SCREEN to calculate the maximum ground-level ambient air concentrations due to the strippers. Table 4-8 contains the results from using SCREEN, however, it does not contain much information to be useful. For example:

- a) There is no information on where the maximum ground-level ambient air concentrations occurred. The maximum ground-level concentrations may have occurred onsite or offsite.

- b) The report did not contain the range and extent of the ground-level concentrations.
- c) The three air strippers are located in different locations. There is no information on how the range of ambient air concentrations overlap.

The PRPs used the combined maximum ground-level concentrations from all three uncontrolled air strippers to calculate residential risk. This is extremely conservative since one of the strippers is approximately 2500 feet away from the other strippers, and the air strippers do have controls. However, the Feasibility Study did not contain enough information to evaluate the emissions from the strippers properly. To perform the analysis in-house, the following information pertaining to each individual air stripper will be necessary:

- a) total influent liquid flowrate,
- b) concentration of species i in influent water,
- c) stripper or stack height,
- d) stripper or stack inside diameter,
- e) exit gas velocity,
- f) exit gas temperature,
- g) stripping efficiency,
- h) base elevation of the strippers,
- i) base elevation, dimensions and location (preferably in UTM coordinates) of nearby structures (for downwash calculations),
- j) location of the stripper (preferably in UTM coordinates),
- k) location of nearby residents,
- l) location of the fence line of the site in relation to the air stripper, and
- m) unusual terrain near the site.

If the PRPs have more information on the air dispersion modeling analysis they performed, they should submit this information for evaluation.

Question 2 - Actual pre- and post-filter air emissions samples appear on Table 4-2 of the report. Could these concentrations be used in an estimate of receptor concentrations? Are they more or less appropriate than the SCREEN concentrations? If appropriate, would they be higher or lower than the SCREEN concentrations?

The pre- and post-filter air emissions samples that appear on Table 4-2 are concentrations of contaminants in the stripper exhaust. These measurements are not ambient air concentrations. At best they can be used to determine the possible worst case ambient air concentrations of the contaminants at the stripper locations - such as what would occur if a low-lying pipe ruptured. The pre-filter concentrations should be much higher

than any concentrations obtained by the SCREEN model. The concentrations post-filter may or may not be higher than the SCREEN model results of uncontrolled stripper emissions. Most of the contaminants on the post-filter samples should be significantly reduced by the carbon filter. However, the air emission samples do show that certain compounds such as vinyl chloride, freon 12, and 1,1-dichloroethane may not be effectively attenuated by the carbon filter.

Overall, Alternative #5 is acceptable from an air perspective. Alternative #5 includes excavation, incineration, return of the ash to the landfill, and air stripping with carbon adsorption. If this Alternative is selected, during excavation, the workers should be outfitted with appropriate protective gear and personal air monitoring should be performed.

#### C. EPA Hydrogeologist:

Most of the Hydro's previous comments have been addressed, except for a few:

1. First, while there is no proof contained in the Remedial Investigation (RI) that current off-site contamination is related to the flushing of contaminants in the vadose zone, contaminant concentrations appear to be decreasing. This may be due to natural degradation and the reduction of contaminant migration resulting from the extraction wells. To enhance the cleanup of the off-site wells, it is suggested that, if feasible, the current extraction discharge rates be increased to levels that will actively extract contaminated ground water from the Paules well. Alternatively, an additional well could be drilled north of the landfill. The appropriate location to be determined during the Remedial Design stage.
2. Second, the issue of the cap is not adequately addressed. Contrary to the PRP's argument, some details on the cap will be needed for adequate costing purposes. Also, the issue of testing the chemical integrity of the cap, should clays soils be used, will need to be addressed. The acid-generating capacity of these soils will also need to be examined. Please see enclosed Regional Fact Sheet and a recently published paper on the issue.
3. Finally, the PRP's will need to provide EPA with their modeling parameters and results for the HELP II and MULTIMED models. Please note that the parameters listed for the RUST model (p. C-11) may not completely satisfy model requirements for the HELP or MULTIMED models. Also, the calculations showing the decrease of 65% of the ground water gradient due to capping should be provided. It is also

necessary to explain how MULTIMED was used to predict the time for the vadoze zone concentrations beneath the landfill cells to reach background concentrations given that the concentrations in the landfill are not characterized.

#### D. EPA's Biological Technical Assistance Group (BTAG) Comments

The Biological Technical Assistance Group (BTAG) has reviewed the May 1994 revised draft Feasibility Study (FS) for the York County Landfill in Stewartstown, Pennsylvania. These comments are offered for use on behalf of EPA and FWS BTAG members.

The BTAG previously commented on the December 1992 Draft FS. Appendix C of the revised draft FS on pages C-34 to C-37 responds to BTAG comments, however, the revised FS sections are not redlined to show changes. This caused the time-consuming task of reviewing the entire document rather than allowing us to concentrate upon only those sections subject to revision. The comments are on the Appendix C response and emphasize areas where we disagree with the response and recommend additions to post-FS activities.

The major disagreement is whether outfall discharges from the operating ground water treatment system are contaminating the receiving surface water and sediment. We disagree with numerous statements in the FS response in support of this position.

First, the outfall concentrations are compared in Table C-5, "Selected Metals Monitored at Outfalls" to U. S. Freshwater Normal Range. We note the reported upper normal range for cadmium and silver, both detected some time during site studies, exceed the chronic Ambient Water Quality Criteria (AWQC) for each metal. The upper range value for lead and mercury exceed their acute AWQC value. We find comparison of site values to such nation-wide range values of little value as we are not given the mean and standard deviation. The arithmetic mean or the lower 95 percent confidence interval estimate for skewed data are the more appropriate and environmentally protective values to consider in such comparisons. Also, we do not know the size and physical setting of the referenced surface waters. We, therefore, recommend final FS and subsequent site studies not make comparisons and decisions relative to national surface water range values, but use regional, and better still, area background arithmetic mean values or the lower 95 percent confidence interval value if the standard error of the mean exceeds 20 percent of the mean value.

It is next stated that arsenic, cadmium, and selenium were not detected in surface water during the RI, but then noted these elements were subsequently detected at the treatment outfalls.

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It is claimed the detected metals were particulate (i.e., total) and not dissolved levels and a summary of outfall levels are given in Table C-5. We find that revised FS Table 1-5, "Results for the Four Water Samples Collected at the York County Landfill on 31 July 1992," show total and dissolved metal levels were both detected for arsenic, lead, mercury, and zinc, and that the levels for each metal's phase are basically equal and with some dissolved levels exceeding totals. Cadmium and selenium were detected in the total phase at only one outfall. Table C-5 should have also included values from the total metal analyses of the two outfalls presented in revised FS Tables 1-7 and 1-8 to give a complete picture. In addition to the range, Table C-5 should have also included the mean and standard deviations.

Even though no detected outfall metal exceeded its acute AWQC, cadmium and mercury exceeded their chronic value. We note the silver detection limit (or is it the quantification limit?) in Tables 1-7 and 1-8 exceeds the acute AWQC. This may help to explain why silver was not reported as detected in any of the outfall samples. The detection and potential for detection of metals are at levels of biological concern (in both total and dissolved phases). Mercury is of special concern, as it is the most consistently detected metal in surface water and sediment and has a very high bioconcentration factor. We recommend that post-FS toxicity testing and monitoring include water toxicity testing and chemical analysis of water and sediment along with sediment toxicity testing. Analysis of the sediment analysis should include total organic carbon (TOC) and grain size for purposes of interpreting results. The analytical methods for water require quantification limits at or below chronic AWQC levels and for sediment at or below the "ERL" sediment guidance values in Long and MacDonald (1992) (see citation at end). Results of the surface water and sediment analytical testing should include the water criteria and sediment guidance values. For silver, we note 0.12  $\mu\text{g/l}$  is the appropriate chronic criteria.

In our prior comments, we expressed concern that any remedial alternative should not degrade existing surface water quality. The response notes the outfalls are permitted under the NPDES program administered by Pennsylvania and then infers, since the discharges are in compliance, that future discharges will protect the area's surface water quality. We are advised that the landfill's current NPDES permit does not include discharge limits for metals. Since NPDES permits must be renewed at 5-year intervals, at which time metal discharge limits may be imposed, it is BTAG's recommendation that the remedial alternatives be designed to meet the most stringent possible metal discharge limit, which would be the chronic AWQC at the end of the outfall pipe.

Since historical data is absent with regard to the volume of

water supplied by the outfalls to the surface waters, it is apparent that the current volume is the base condition. Any reduction in stream flow that results in a permanent loss of stream habitat will require development and implementation of a stream mitigation plan. We, therefore, recommend the post-FS monitoring include assessment of stream habitat with subsequent development of mitigation for any lost stream habitat.

With respect to protecting wetlands from dewatering, if Alternative No 3 is selected and capping occurs, we appreciate the proposal to monitor and reduce withdrawal rates so that the water table beneath the area wetlands will not be lowered. However, we recommend the post-FS monitoring also include direct monitoring of downgradient wetlands for loss of wetland habitat with subsequent development of mitigation for any lost wetland habitat.

When BTAG commented on the wetland delineation, we asked for a more detailed habitat figure than provided in the FS. We again request such a figure to assist the monitoring and development of stream and wetland mitigation plans especially if Alternative No. 3 (the capping alternative) is implemented.

The BTAG comment about expected occurrence of birds was in reference to habitat downgradient of the landfill especially the wetland and stream corridors. We agree that an active landfill has diminished habitat value, but with landfill closure such activity is expected to decrease and with different vegetative replanting and maintenance such wildlife habitat value could be expected to increase. We request that any habitat restoration, mitigation, and maintenance, including the landfill cap, provide resource value to resident and migratory wildlife. We note that Appendix A of the FS (Re: BTAG comments on the RI) has discussed the consideration to provide such wildlife value in Remedial Design (RD).

The response about that impact to Muddy and Deer Creek is unlikely does not address BTAG's concern with the adequacy of characterization of the full possible extent of site contamination downgradient of RI surface water and sediment sample locations. We recommend the post-FS monitoring and assessment incorporate recommendations from previous BTAG comments regarding locating adequate and appropriate surface water and sediment samples. We also note that every recommended surface water and sediment sample (except for the last one) should have at least one more downgradient sample in the next depositional area to ensure the absolute extent of site contaminants is quantified. If the most - downstream station shows site-related contamination, then another station farther down-stream will be needed. With regard to background surface water and sediment sample, as discussed on page C-7, the BTAG May 1993 comment notes an area west of the landfill along Plank Road

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that is in the upper end of Ebaugh Creek beyond SW/SED 3. If this area is judged not appropriate, we next recommend sampling a surrogate watershed of similar physical character in the area beyond the landfill's influence.

Lastly, we note that BTAG's recommended ecologically-related remedial objectives were added to the revised FS on pg. 2-8. With regard to item #6, we recommend rewording so as to anticipate and minimize, to the extent feasible, damage to all area ecological habitat during remediation and to provide habitat restoration or mitigation and maintenance for unavoidable habitat damage.

Long, E.R. and D.D. MacDonald. 1992. National Status and Trends Program Approach. In: Sediment Classification Methods Compendium. EPA 823-R-92-006. EPA Office of Water (WH-556). Washington, D.C.

#### E. RCRA Programs Comments

The FS Report was reviewed by the EPA's RCRA Programs to determine if any RCRA statutory or regulatory requirements are applicable to the York County Landfill Superfund Site's proposed remediation.

RCRA Programs provided previous comments on the YCSL December 1992 DRAFT FS. The information contained within the May 1994 Draft FS does not change the previous RCRA comments. It appears that available information indicates that RCRA is not applicable to the contaminants at YCSL. As noted elsewhere in the EPA comments, RCRA requirements that may be relevant or appropriate, for example a RCRA cap, may be determined by the EPA as design criteria for certain remediation alternatives.

As point of information, the RCRA comments summarized on p. C-31 of Appendix C should be revised. The existing comments indicated that "if" any material and/or contaminated environmental media such as groundwater, were to fail the RCRA TCLP criteria then such material would need to be treated to the characteristic level. This statement will not be accurate after July 31, 1994.

Since the RCRA Programs' commented on the December 1992 FS, EPA issued a proposed rule on Land Disposal Restrictions (LDR) as applicable to TCLP organic wastes in the September 14, 1993 Federal Register (FR) (58 FR 48092). In addition EPA issued an Interim Final Rule on LDR for Certain Characteristic wastes in the May 24, 1994 FR (58 FR 29860), due to a Court decision. Without going into great detail, EPA must issue a Final LDR Rule on treatment standards for TCLP organic waste: (D018-D043) by July 31, 1994. This rule will require that any material that

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fails the TCLP organic levels must be treated to levels that in most cases are well below the level that subjected the material to RCRA and will be measured by a total, not a TCLP level, and in addition must also address any other underlying hazardous constituent in that material;. The informational point is that if a material fails TCLP, treatment to below the TCLP level will no longer meet RCRA requirements. RCRA and LDR will be far more stringent in this area. The probable effective date will be mid-November 1994. (EPA RPM's Note: If the effective date for this RCRA requirement is later than the date that the ROD is signed, this requirement will not apply. On the date that the ROD is signed by the EPA Region III Regional Administrator (RA), only the ARARs that are in effect on that date will apply, thus ARARs are frozen by the ROD signing.)

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EPA  
Region III

Technical Fact Sheet  
Design of Clay Caps

## PROBLEMS ASSOCIATED WITH THE USE OF SULFIDE-BEARING CLAYS AS CAPS FOR LANDFILLS

by  
DAVID M. KARGBO, PH.D.

Hazardous Waste Management Division  
Office of Superfund Programs, Technical Support Section  
May 1993

### INTRODUCTION

This fact sheet provides rationale for the need to test the acid-generating capabilities of potential clay cap materials before they are used to cap landfills. Currently, the only regulation for the use of clay soils as caps is that upon compaction, at appropriate moisture levels, they should provide extremely low saturated hydraulic conductivity ( $K_s$ ) values ( $< 10^{-7}$  cm/s or  $< 1$  inch per year). Much attention on the use of clay soils in landfill settings has been focused on the effects of the physico-chemical interactions between the clay components and the infiltrating pollutants when the clay soil is used as a liner. With respect to clay soil in landfill caps, it has been assumed that infiltrating water will have little or no influence on the integrity of the cap. Unfortunately, this has led to the indiscriminate use of clay soils, including sulfidic (sulfide-bearing) clays, to cap landfills. Sulfidic clay soils have the potential to generate extreme acidity, resulting in increase in the permeabilities of the clay covers to percolating moisture, enhancement of metal mobility to ground water, erosion of the clay covers, killing of vegetation on downslopes of the landfill covers, and environmental degradation of receiving streams (Figure 1).

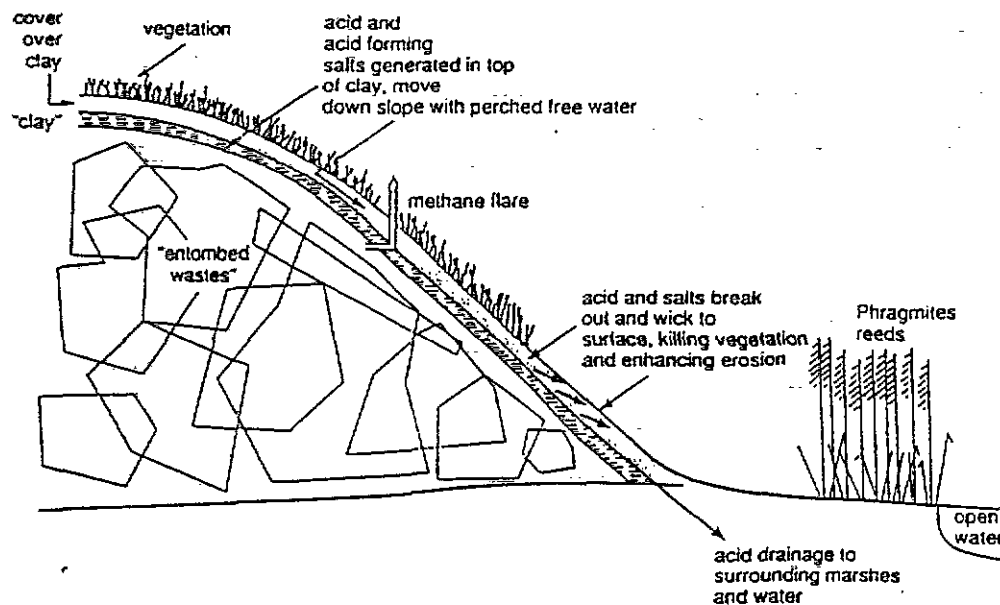


Fig. 1. Idealized landscape cross-section of a landfill with sulfidic "clay" cap showing probable detrimental consequences (Kargbo, et al., 1993)

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## MECHANISM OF SULFIDIC MATERIAL FORMATION & ACID GENERATION

Sulfidic materials occur in clays mainly as pyrite ( $\text{FeS}_2$ ) which formed in ancient reducing environments such as marshes. In these environments, the sulfate ( $\text{SO}_4^{2-}$ ) in sea water is reduced to sulfide, and iron ( $\text{Fe}^{2+}$ ) from free iron oxides in sediments is reduced to  $\text{Fe}^{2+}$ . When exposed to the air, pyrite is oxidized. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is eventually formed as rain water comes in contact with the oxidized pyrite in the capped soils:



## OCCURRENCE OF SULFIDIC CLAYS

Due to their mode of geologic formation, the majority of clay soils with sulfidic materials are found in Coastal Plain and marsh areas. However, upland sulfidic clay soils have been reported in the literature. Observed acidity problems associated with surface-mining areas constitute evidence of the occurrence of these soils in upland areas as well. Sulfides associated with upland sedimentary clay deposits appear to have formed mainly by similar processes in the geologic past at the time that the clayey sediments accumulated. The Cretaceous lignitic clays in New Jersey (which are commonly used for capping landfills and which have demonstrated the above problems) are examples of such deposits.

## IDENTIFICATION & TESTING FOR SULFIDIC CLAYS

It is suggested that cap designers test the acid-generating capabilities of potential clay cap materials before exploiting these earth formations. Acid sulfide bearing soils, in a moist condition, are usually of dark color, but occasionally range to light grey. Consequently, clayey materials that are grey or black with essentially no chroma and low values by the **Munsell** terminology should definitely be tested. This can be done by incubating a sample of the candidate capping material (with  $\text{pH} > 3.5$ ) as a layer, 1 cm thick, under moist aerobic conditions (field capacity) and at room temperature. The soil will be said to contain sulfidic materials if it shows a drop in pH (1:1 by weight in water or in a minimum of water to permit measurements) of 0.5 or more units to a pH value of 4.0 or less within 8 weeks. The material should be repeatedly wetted and dried over the measurement period. This method was used to demonstrate the presence of sulfidic materials in the clay soils used to cap the Fresh Kills landfill in New York (Figure 2).

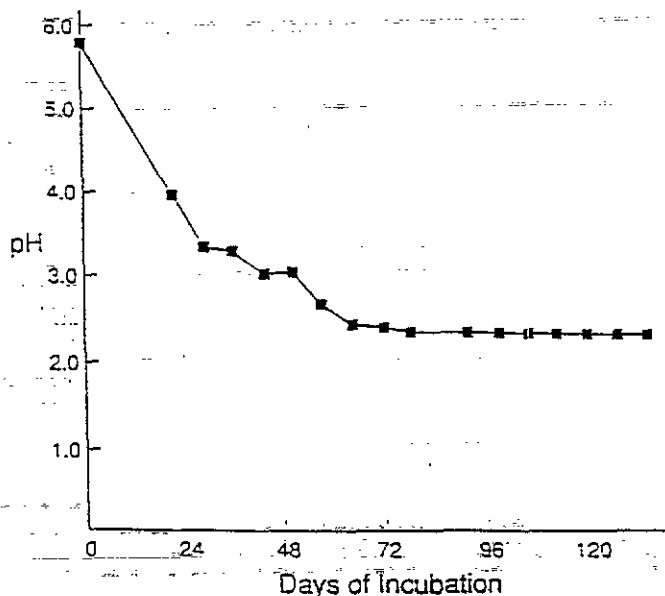


Fig. 2. Graph of pH vs. time of incubation for sample of landfill cap clay from Fresh Kills landfill on Staten Island, New York (Kargbo, et al., 1992)

The technical basis for the above test is the recent definition of sulfidic materials published (after extensive peer review within the scientific community) in *Keys to Soil Taxonomy* (1992).

If the candidate capping material is found to contain sulfidic materials, decisions should then be made as to whether the soil should be avoided or used with amendments to the cap design.

## ADDITIONAL INFORMATION

For more information, please contact Dr. David M. Kargbo, Superfund Technical Support Section at (215) 597-6488.

AR301836

D. M. Kargbo · D. S. Fanning · H. I. Inyang · R. W. Duell

## Environmental significance of acid sulfate “clays” as waste covers

Received: 4 March 1993 Accepted: 9 March 1993

**Abstract** The current regulatory requirement for cover soils in landfills and surface impoundments is that the soils attain, upon compaction, a very low hydraulic conductivity of  $10^{-7}$  cm/s or less. Although the influence of the interaction between waste chemicals and clay soil on waste migration has been extensively studied, attempts to incorporate as design components the effects of sulfidic (sulfide-bearing) clays on the integrity of clay caps have largely been ignored. These influences may include increasing the permeability of the cover to percolating moisture, enhancing erosion of clay covers, and killing of vegetation on downslopes of the cover. Consequently, it is suggested that clay cap designers test the acid-generating capabilities of potential clay cap materials before exploiting these earth formations. This can be done by incubating a sample of the candidate capping material (with pH > 3.5) under moist aerobic conditions (field capacity) at room temperature. The soil will be said to contain sulfidic materials if it shows a drop in pH (1:1 by weight in water) of 0.5 or more units to a pH value of 4.0 or less within eight weeks. Decisions should then be made as to whether the soil should be avoided or used with amendments to the cap design.

**Key words** Waste covers — Surface impoundments — Waste migration

D. M. Kargbo (✉)  
US Environmental Protection Agency (3HW13), 841 Chestnut Bldg.,  
Philadelphia, Pennsylvania 19107, USA

D. S. Fanning  
Department of Agronomy, University of Maryland, College Park,  
Maryland 20742, USA

H. I. Inyang  
US Environmental Protection Agency, Office of Solid Waste  
(OS-5303W), Washington, DC 20460, USA

R. W. Duell  
Crop Science Department, Cook College, P.O. Box 231, New Brunswick,  
New Jersey 08093, USA

### Introduction

Subtitle C of the Resource Conservation and Recovery Act (RCRA) requires the US Environmental Protection Agency (EPA) to establish a federal hazardous waste management program that would ensure that hazardous wastes are safely handled from generation until final disposal. Under Subtitle C of RCRA, EPA issued a series of hazardous waste regulations that are published in Chapter 40 *Code of Federal Regulation* (CFR), Parts 260–265, and Parts 122–124. Regulations for the land treatment, storage, and disposal (LTSD) of hazardous wastes are contained in Chapter 40 CFR Part 264, which established performance standards for hazardous waste landfills, land treatment units, and waste piles. To implement the regulations, EPA has prepared documents for use by preparers and reviewers of permit applications for hazardous waste LTSD facilities. These documents include technical guidance documents, permit guidance manuals, and technical resource documents (US EPA 1982a,b, 1986, 1988). While some of these documents recognize the significance of the influence of the soil chemical properties on waste migration in the environment, no attempt has been made to study the problems associated with the use of sulfide-bearing clays or other soil materials as covers in numerous landfills and surface impoundments across the country. If, for example, the sulfuric acid potential of acid sulfate clays were calculated, they would be classified as toxic and hazardous. However, much more attention has been paid to the effects of geomaterial–pollutant physicochemical interactions in the liner components than to the covers of landfills. The justification for focusing attention on liners has been that liners underlie contained wastes whose percolating leachates can easily contact these liners.

Certain clayey soil materials are used as caps because upon compaction, at appropriate moisture levels, they can give extremely low water hydraulic conductivity ( $K_{sat}$ ) values ( $<10^{-7}$  cm/s or  $<1$  in./yr) required by environmental regulations and because alternative materials that provide the appropriate  $K_{sat}$  are usually not available at reasonable

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Fig. 1. Migration of soil solutions of pH < 4 killed established vegetative cover at the foot of this landfill side-slope where 12 in. (30 cm) of limed topsoil had been placed over an equal depth of acid sulfate clay approximately 4 y. prior



cost. In some areas where these clays have been used as landfill caps, extreme acidity problems and devegetation have been reported at the foot of 4:1 slopes on the sides of the landfills (Fig. 1).

The objective of this paper is to increase the awareness of environmental professionals to the occurrence of acid sulfate soils; discuss their environmental effects, especially on the durability of waste containment system components; suggest a simple method to test for their presence; and provide a rationale to support a modification of the hazardous waste regulation for landfill and surface impoundment covers that might utilize soil materials that could be classified as acid sulfate soils.

### Occurrence and formation

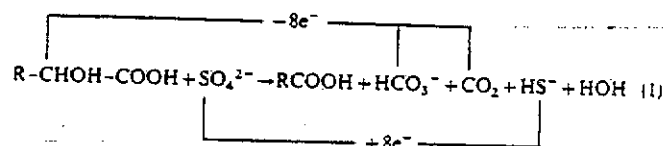
Acid sulfate soils may be defined as those soils in which sulfuric acid (formed by the oxidation of pyrite,  $\text{FeS}_2$ , or rarely, of other reduced sulfur compounds), has been, is being, or may be produced in amounts that have lasting effects on principal soil characteristics. Due to their mode of geologic formation, the majority of potential acid sulfate soils are found in coastal plains and marsh areas. However, upland acid soils have been reported in the literature. Observed acid sulfate soils along road cuts, ditches, and associated with surface-mining areas constitute evidence of the occurrence of these soils in upland areas as well.

The formation of acid sulfate soils involves two gross processes: sulfidization and sulfuricization (Fanning and Fanning 1989).

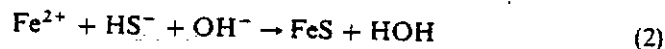
### Sulfidization

Sulfidization is the accumulation of sulfides primarily in soils and sediments along ancient sea coasts where rich sources of sulfur (about 900 ppm S), mainly as sulfate sulfur, exist in seawater compared to the low S content of

most inland "fresh" waters. Sulfate-bearing waters come in contact with tidal marsh soils and submerged sediments by the action of waves and tides. In the process of oxidation of organic matter, from which they derive their energy, bacteria living in such saturated, anaerobic environments reduce the sulfate ( $\text{SO}_4^{2-}$ ) to sulfide by using the  $\text{SO}_4^{2-}$  as an electron sink, accepting electrons released in the oxidation of the organic matter (equation 1):



Iron ( $\text{Fe}^{3+}$ ) from free iron oxides (e.g.,  $\text{Fe}_2\text{O}_3$ ) in sediments is also reduced to  $\text{Fe}^{2+}$ . The  $\text{Fe}^{2+}$  in turn may react with the sulfide (as  $\text{HS}^-$ ) to form a ferrous sulfide ( $\text{FeS}$ ) precipitate (equation 2).



The reaction may proceed to form griegite ( $\text{Fe}_3\text{S}_4$ , equation 3a) and pyrite ( $\text{FeS}_2$ , equation 3b).



Alternatively, a number of studies have shown that direct formation of pyrite without the formation of monosulfides, as suggested in the scheme presented here, may take place. Sulfidization is summarized graphically in Fig. 2.

When a soil classified as clay (from USDA Soil Classification System) is subjected to the above reaction, the resulting soil material is a sulfidic clay.

The progressive depletion of pore water sulfate with depth in sediments from a soil core in Carmen Basin (Fig. 3) has been provided as evidence (Goldhaber and Kaplan

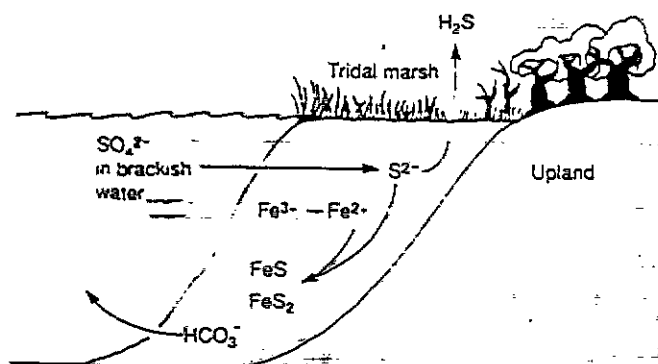


Fig. 2. Diagram illustrating sulfidization (after Fanning & Fanning, 1989)

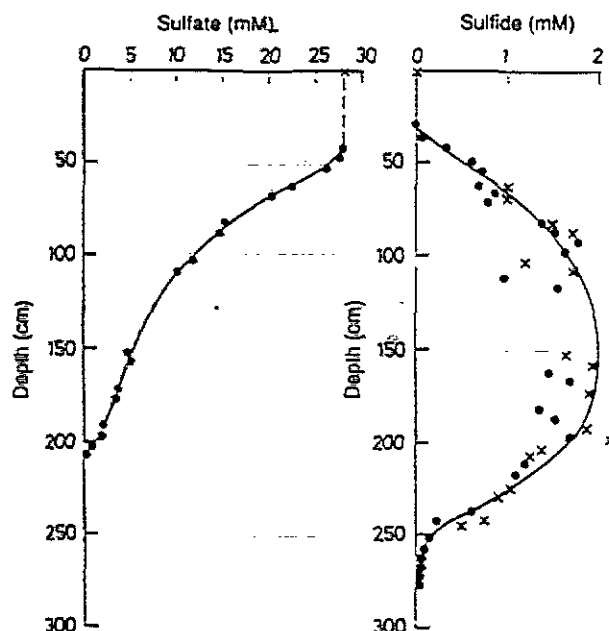


Fig. 3. Plot of dissolved sulfate and sulfide in pore waters of a core from Carmen Basin, Gulf of California (after Goldhaber & Kaplan, 1982)

1982) for the in situ bacterial sulfate reduction during sulfidization. This decrease is associated with an expected initial increase in dissolved sulfide as sulfide is generated and as sulfide production rate exceeds sulfide removal rate to form pyrite. As sulfate decreases to zero concentration, the production of sulfide from sulfate ceases, so that below the depth of zero sulfate, dissolved sulfide decreases.

Organic matter (as an electron donor) is required in the sulfur reduction process. Consequently, it has been demonstrated that the sulfur content of tidal marsh soils increases with an increase in organic matter content (Darmody and others 1977). Furthermore, for a variety of sedimentary environments and depths within the sediment column, Sweeney (1972) reported that the percent reduced sulfur increases with increase in organic matter (Fig. 4).

Evidence about the presence of pyrite in acid-producing soils used as landfill covers was provided by Fanning

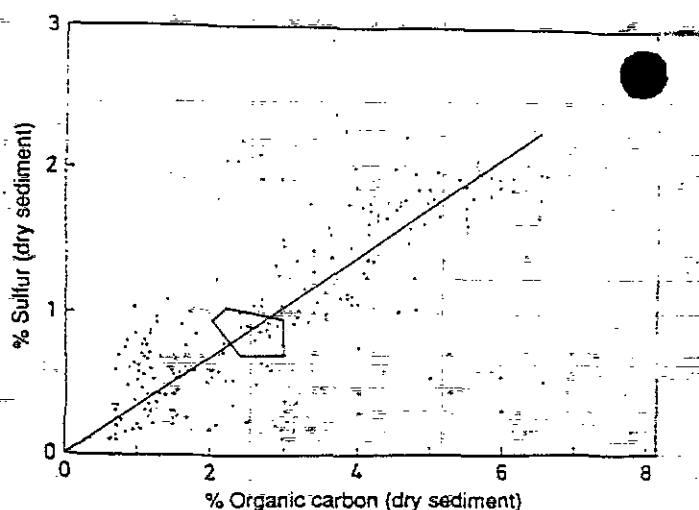


Fig. 4. Plot of percent reduced sulfur vs. organic carbon content (after Sweeney, 1972)

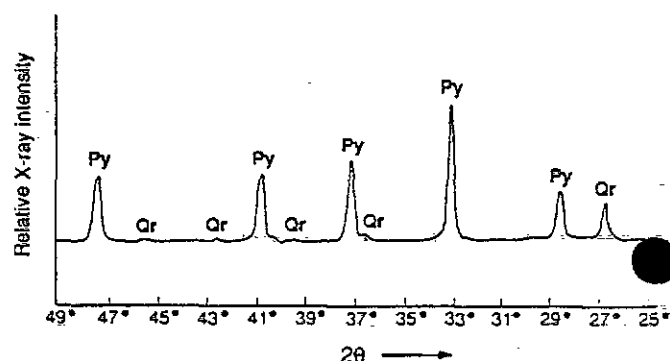


Fig. 5. X-ray diffraction pattern prepared with Cu K alpha X-rays showing the presence of pyrite (Py) and quartz (Qr) in powdered "marcasite nugget" from "clay" used for cover for Edgeboro Landfill in New Brunswick, New Jersey (redrawn from Fanning, 1991)

(1991), who attempted to determine whether the material used to cap the Fresh Kills landfill on Staten Island, New York, could be classified as a sulfidic material. By x-ray spectroscopy, the material was found to contain 2.9 percent S (on an air-dry basis). Fanning (1991) also examined a sample of cover "clay" soil from the Edgeboro landfill in New Brunswick, New Jersey, using x-ray diffraction and confirmed the presence of pyrite (Fig. 5).

The pyrite formed in the acid-sulfate clays we have surveyed is a type called "marcasite" (Fig. 6). This mineral forms smaller cubic crystals than those in the "fool's gold" found in the mid-western states. The presence of "marcasite nuggets", most readily found in rills and furrows, is a sure sign of (potentially) excessive acid conditions. The "marcasite" may, however, also occur in tiny free crystalline form, in which case it may reflect light like fine particles of mica.

Acid sulfide-bearing soils, in a moist condition, are usually of dark color, but occasionally range to light gray. When dry, these fine-textured soils are lighter in color and may become very dusty when disturbed, as by vehicular traffic.

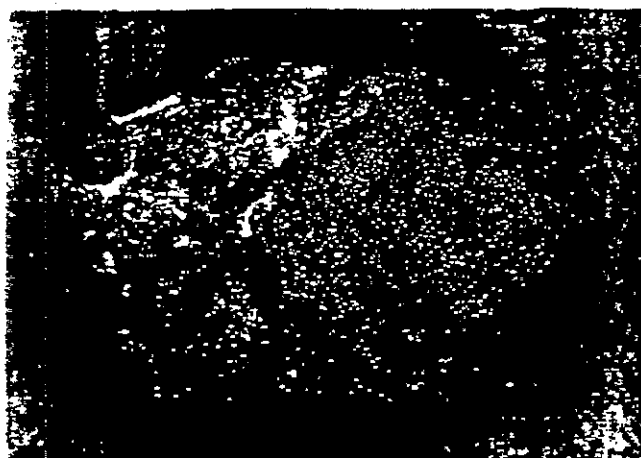
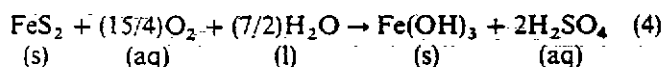


Fig. 6. A relatively durable nugget of marcassite showing at least 3 crystalline types. It disintegrated after 15 yr. of exposure in an indoor environment

Sulfides associated with upland sedimentary clay deposits appear to have formed mainly by similar sulfidization processes in the geologic past at the time that the clayey sediments accumulated. The Cretaceous lignitic clays in New Jersey (which are commonly used for capping landfills) are an example of such deposits.

#### Sulfuricization

Sulfuricization is the process by which sulfidic soil materials are oxidized, resulting in the production of sulfuric acid. The overall process of pyrite oxidation resulting in the formation of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is given in equation 4 as:



where "s," "l," and "aq" represent solid, liquid, and dissolved species, respectively. The process is, however, more complicated than indicated in this overall reaction. It involves several types of redox reactions, hydrolysis, complex ion formation, solubility controls, microbial, and kinetic effects. For example, Nordstrom (1982) reported that although oxygen is the overall oxidant for pyrite oxidation, the fundamental mechanism and major rate-determining step(s) may not involve oxygen.

Fanning and Fanning (1989) described three idealized stages in the sulfuricization process: presulfurization, active sulfuricization, and postsulfurization.

Presulfurization refers to conditions that represent potential acid sulfate soils. These soils include any sulfide-bearing materials in which oxidation of the sulfides has been prevented, for example, by continuous saturation with water. Materials representing this stage may form by sulfidization, which may be either actively on-going or may have gone on in the geological past with the material protected from previous oxidation by anaerobic burial.

During active sulfuricization, the sulfide-bearing mate-

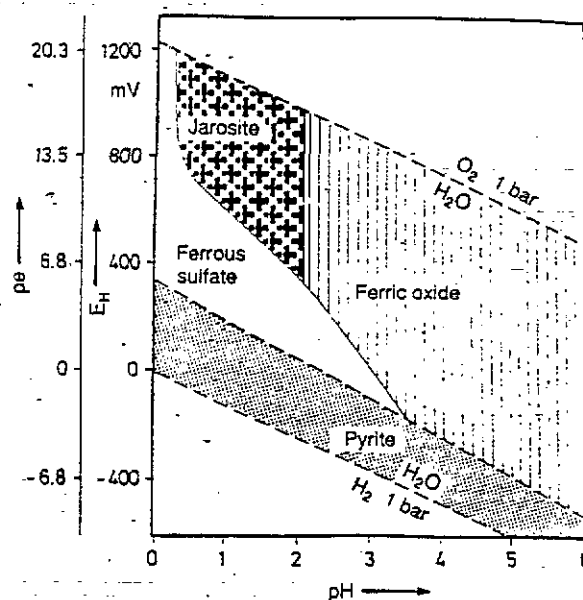


Fig. 7. Eh-pH diagram showing stability fields for oxidation-reduction-sensitive constituents found in acid sulfate soils under certain assumed boundary conditions. Conditions are  $p\text{Fe} = 4$ ,  $p\text{SO}_4 = 2.3$ , and  $pK^+ = 3.3$  (after Fanning & Fanning, 1989)

rial is exposed and undergoes oxidation. When carbonates are not present and sulfuric acid is being produced more rapidly than it can react with silicate minerals, horizons may form that are called sulfuric horizons if the pH drops to 3.5 or less. Quite frequently, jarosite [ $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ], a yellow secondary mineral, is found in these sulfuric horizons. In some sulfuric horizons, however, the Eh may be high enough to generate high acidity but not high enough to form jarosite (Fig. 7), which requires conditions oxidizing enough for  $\text{Fe}^{3+}$  to be stable.

Under conditions represented in Fig. 7, Fanning and Fanning (1989) show that if iron is completely oxidized and hydrolyzed to ferric oxide or equivalent form,  $[\text{Fe}(\text{OH})_3]$  then each mole of pyrite,  $\text{FeS}_2$ , will generate two moles of sulfuric acid (equation 4). However, complete oxidation and hydrolysis may not occur, and the acidity generated may be less than indicated by equation 4.

During postsulfurization, sulfuric acid has been generated in large amounts in the past, but the present rate of acid generation is negligible. The resulting pH is typically 4 or above. Soil materials representing postsulfurization are sometimes recognized by the presence of minerals such as jarosite, in materials with a pH too high for a sulfuric horizon. Such jarosite presumably formed during the active stage but remains in the soils for long periods after the active sulfuricization has ceased. Commonly, soil materials representing the active and presulfurization stages underlie materials that represent the postsulfurization stage (Fanning and others 1993). These soil materials that underlie materials that represent the postsulfurization stage may give rise to new active acid sulfate soils when exposed to future oxidizing conditions. For example, Fanning and Fanning (1989) and Wagner and others (1982) reported the



Table 1. General regimes of permeability increases of clayey soils permeated by various nonorganic pollutants (values are nonexact due to variability in soil gradation and mineralogy)

Acid pollutant	Concentration	Increase ratio	Material	Reference
Acid mine drainage HCl	pH $\approx$ 3	<2	S-B <sup>a</sup> Backfill	D'Appolonia (1982)
	0.36%	11.8	Bentonite	Pavilonsky (1985)
	0.36%	2.7	Kaolinite	Pavilonsky (1985)
	1.00%	3.0	S-B Backfill	D'Appolonia (1982)
	3.65%	15.2	Bentonite	Pavilonsky (1985)
HNO <sub>3</sub>	3.65%	5.0	Kaolinite	Pavilonsky (1985)
	0.7%	1.6	Kaolinite	Pavilonsky (1985)
	0.7%	16.3	Bentonite	Pavilonsky (1985)
	7.0%	7.4-11.9	Bentonite	Pavilonsky (1985)
	1.0%	<2	S-B Backfill	D'Appolonia (1982)
H <sub>2</sub> SO <sub>4</sub>	5.0%	1.4	Loam, P1-15	Pavilonsky (1985)
	5.0%	10.3	Bentonite	Pavilonsky (1985)
CH <sub>3</sub> COOH	6.0%	0.8	Loam, P1-15	Pavilonsky (1985)
	6.0%	5.6	Bentonite	Pavilonsky (1985)
	6.0%	5.6	Bentonite	Pavilonsky (1985)
Strong acids (general)	pH < 1	>5	S-B Backfill	D'Appolonia (1982)
Weak acids (general)	pH > 1	<2	S-B Backfill	D'Appolonia (1982)

<sup>a</sup> S-B = Soil-Bentonite mixture

development of active acid sulfate soils from exposure of material underlying postactive acid sulfate soils by highway or other construction activities.

#### Potential long-term degradation of landfill covers

It is normally assumed that moisture that may infiltrate through landfill cover soils is essentially neutral in chemistry. This assumption is justifiable in the case of soils with negligible concentrations of soluble materials. However, for acid sulfate clays, the concentration of dissolved compounds in the pore fluid of the soil cover systems may be high enough to induce a physical response of the clayey soil fabric. Such a response can be manifested as an increase in permeability of the clay cap to percolating moisture.

There are two principal ways by which such a physico-chemical interaction may be induced in acid sulfate soils. In the first case, the acidic leachate generated may dissolve soil constituents if its pH is sufficiently low. The enlargement of flow channels would increase the permeability of the soil barrier layer. The significance of dissolution phenomena to the physical response of soils has been described by Lukas and Gnaedinger (1972). Cases in which the permeability of earthen materials has increased due to contact with acidic fluids of various concentrations have been described by D'Appolonia (1982) and Pavilonsky (1985). Relevant information is provided in Table 1.

Cation exchange phenomena may also cause an increase in the permeability of acid sulfate soils in landfill covers. As explained earlier, the sulfidization process often causes the production of iron sulfide-bearing compounds, which upon oxidation may result in increased acidity and the formation of iron-containing compounds. Usually, such soils may also contain significant proportions of sodium montmorillonite. Because iron is higher in the electrochemical series than sodium, the latter is more likely to be replaced. It is commonly observed that replacement

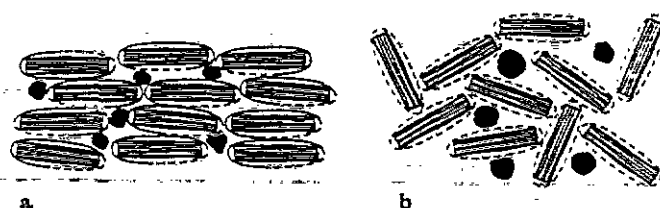


Fig. 8. a Parallel structure of clay particles due to large diffuse double layers and b flocculated structure of clay particles due to reduction in thickness of diffuse double layers

of monovalent cations by polyvalent cations results in a shrinkage of the double layer that surrounds clay particles. The net result is frequently a transformation of the clay structure from an originally dispersed pattern to a flocculated pattern. Flocculated clays usually exhibit higher vertical permeabilities than dispersed clays. Both structures are depicted schematically in Fig. 8.

Using the Guoy-Chapman theory, the thickness of the diffuse double layer that surrounds each clay particle can be related to other physical and chemical parameters as shown in equation 5.

$$t = \frac{DKT}{8\pi N_0 e^2 v^2} \quad (5)$$

where  $t$  = thickness of the double layer;  $D$  = dielectric constant of the permeating fluid;  $T$  = absolute temperature;  $N_0$  = ion concentration;  $e$  = unit electronic charge;  $v$  = valence of the cation; and  $k$  = Boltzmann's constant.

The constriction of the double layer distorts the force equilibrium among the clay particles such that attractive forces exceed repulsive forces, as illustrated in Fig. 9. The situation illustrated in Fig. 8b probably occurs due to a shift in pore-size distribution from small to larger pores at relatively constant porosity. Furthermore, the increase in vertical permeability can conceptually be considered to occur at the expense of horizontal permeability. The risk is that in landfill cover soils that contain high proportions

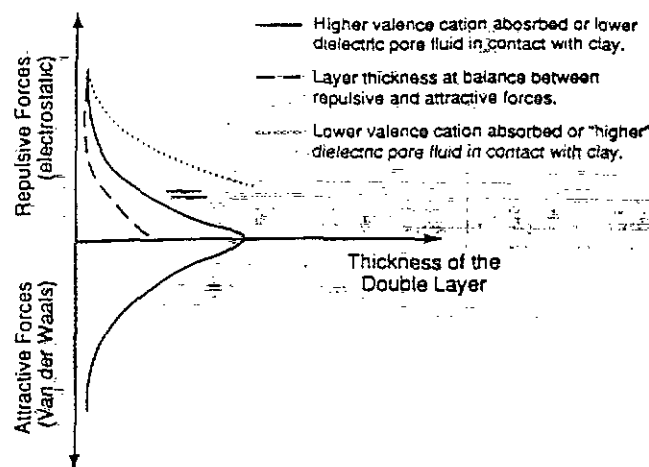


Fig. 9. Effects of cation valence and pore fluid dielectricity on inter-layer spacing

of acid sulfate materials, long-term physicochemical interactions may result in an increase in vertical hydraulic conductivity beyond the maximum limit of  $10^{-7}$  cm/s specified by the US EPA. Dunn (1983) has investigated the effects of acidic fluid generated from lead-zinc tailings on the permeability of clay soils. His experimental results are consistent with the fundamentals discussed above.

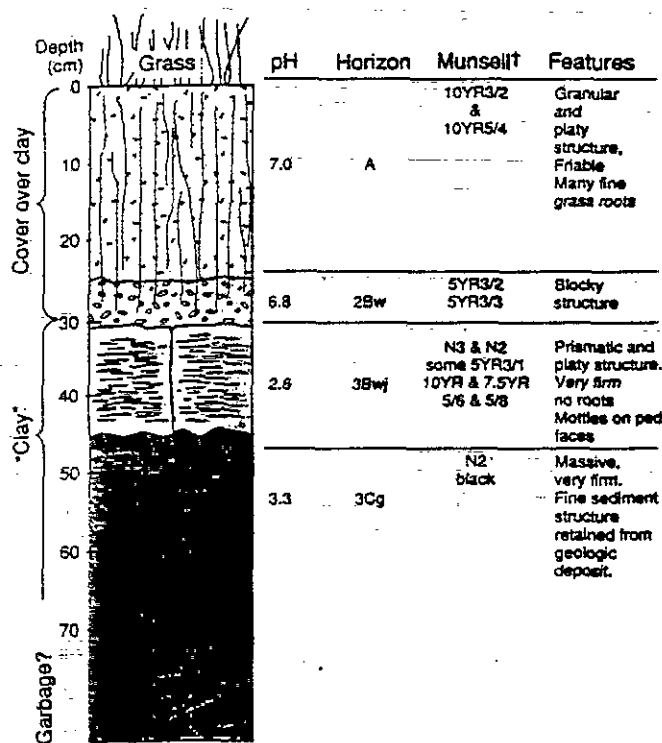


Fig. 10. Diagram of soil profile examined in 2-3 year old cover on the Edgeboro Landfill (redrawn from Fanning, 1991). †: The Munsell notations correspond to the following moist colors: 10YR3/2 = very dark grayish brown; 10YR5/4 = yellowish brown; 5YR3/2 & 3/3 = dark reddish brown; N3 = very dark gray; N2 = black; 10YR5/6 & 5/8 = yellowish brown; 7.5YR5/6 & 5/8 = strong brown

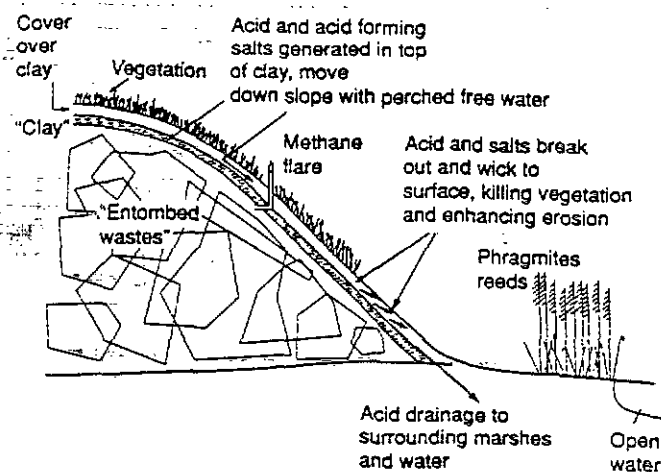


Fig. 11. Idealized landscape cross-section of a landfill with sulfidic "clay" cap showing probable detrimental consequences (redrawn from Fanning, 1991)

A diagram of a soil profile of the Edgeboro landfill showing the influence of pyrite on soil acidity at the landfill is given in Fig. 10. Also observed in this figure is the development of a soil structure probably due to shrinkage of the double layer surrounding the clay particles that contained acid sulfate-bearing materials. Alternatively, cracking could have resulted from desiccation or from differential settling of wastes (subsidence). Such cracking presumably promotes the sulfurization process because it enhances the ability of gaseous or dissolved oxygen to get to the sulfides to oxidize them.

Figure 11 is an idealized landscape cross section of a landfill with a sulfidic clay cap in which acid and acid-forming salts are generated in the top portion of the clay. Carried by perched free water, the acid and acid-forming salts move down slopes, breaking out at the surface or footslopes with the resultant enhancement of erosion, killing of vegetation, and acid runoff draining to surrounding marshes and water. As indicated in Fig. 1, even the addition of lime on topsoil may not prevent the killing of vegetation.

The removal of a stockpile of acid sulfate clay (Woodbury) from the top of Edgeboro landfill was observed to cause a depression one year after removal (Fig. 12). Another year later, the residual activity of soil and water both registered pH 2.5. The area remained devoid of weeds, and birds were never seen in or heard near the pond that developed after rainy periods. Other depressions in the intermediate cover of the active landfill continually abounded with seagulls.

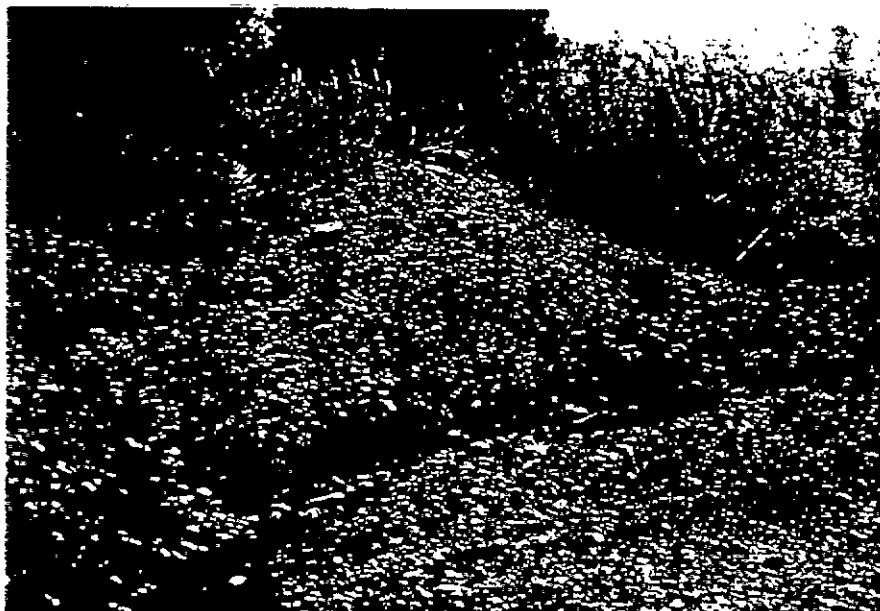
#### Other environmental aspects of acid sulfate soils

Studies of acid sulfate soils have concentrated on salt water and marsh environments, some of which have been artificially drained. However, acid sulfate soils have been reported on sulfide-bearing materials exposed by road build-

Fig. 12. The depression on top of a landfill left by a clay stock pile acidified the soil of the intermediate cover and the water that accumulated following rains to a pH of 2.5. For years, plants would not grow there, and birds would not go in the water



Fig. 13. On a 5° slope, 12 in. (30 cm) of topsoil had eroded away and gullies are deepening in the in-situ-clay. Grass in upper right is little bluestem (*Andropogon scoparius*, very acid tolerant) which has replaced a conventional cool-season mixture of roadside grasses sown 9 yr. prior

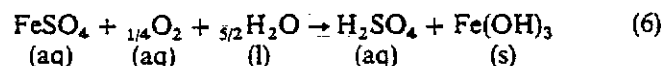


ing. Bare-soil areas on roadside cut-banks illustrate the vegetation-killing capacity of exposed and oxidized acid-sulfate soils (Fig. 13).

Sulfidic dredged sediments have also been reported. For these soils, sulfuric acid can be produced in quantities beyond the capacity of acid-neutralizing substances in the soil to neutralize the acid. Extreme acidity and sometimes associated salinity (e.g., McMullen 1984; Fanning 1993) develop to such an extent that plants cannot survive on these soils.

In mining processes, intermediate products (such as ferrous sulfate) from oxidation of pyrite are frequently formed from oxidizing materials (e.g., mine spoils). During

transport to streams, ferrous sulfate can also undergo oxidation and hydrolysis to form iron "oxide" and generate acidity (equation 6).



These acid waters in streams with precipitates of iron oxide coatings on stream channels are commonly referred to as acid mine drainage. Such waters are capable of killing vegetation and aquatic fauna along their way and mobilize metals carried not just to surface waters but to groundwater as well.

### Testing for presence of sulfidic materials

Fanning (1991) measured the initial pH of the material used to cap the Fresh Kills landfill to be 5.8. Aerobic incubation of the soil caused the pH to drop to 2.4 in about six weeks. The pH remained at this level with continued incubation (Fig. 14). A recent new definition of sulfidic materials in the Keys to Taxonomy by the Soil Survey Staff (1992) provides a basis to test for the presence of these materials. It involves incubation of the material as a layer 1 cm thick under moist aerobic conditions (field capacity) at room temperature. Measurements of pH (1:1 by weight in water or in a minimum of water to permit measurement) should then be made over an eight-week period (usually as the material is repeatedly wetted and dries). The soil materials will be considered sulfidic if they show a pH drop of 0.5 or more units to a pH value of 4 or less within the eight-week period. As indicated earlier, sulfidic materials typically are grey or black with essentially no chroma and low values by Munsell terminology (Fanning and others 1993). Clayey material of such colors are ones that definitely should be tested by incubation tests to see if they qualify as sulfidic.

### Conclusions

Acid-producing soils have been, and continue to be, used as covers in landfills and surface impoundments since the only regulatory requirement specified is the attainment, upon compaction, of a very low hydraulic conductivity. The influence of these soils is far-reaching and may include the increase in permeability of the cover to percolating moisture, the enhancement of erosion of clay covers, and the killing of vegetation on the cover and downslopes and pollution of runoff waters. It is suggested, therefore, that clay cap designers test the acid-generating capabilities of

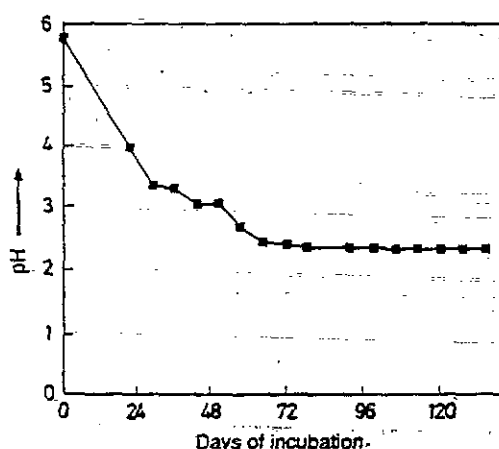


Fig. 14. Graph of pH vs. time of incubation for sample of landfill cap "clay" from Fresh Kills landfill on Staten Island, New York (redrawn from Fanning, 1991)

potential clay cap materials taken at the source, by incubating a sample of the candidate cover soil (with pH > 3.5) under moist aerobic conditions (field capacity) at room temperature. The soil will be said to contain sulfidic materials if it shows a drop in pH (1:1 by weight in water) of 0.5 or more units to a pH value of 4.0 or less within eight weeks. Decisions should then be made as to whether the clay soil should be abandoned (the more environmentally sound decision) or used with amendments to overcome the acidity and associated problems.

**Note** Although some of the authors of this article are employees of the United States Environmental Protection Agency, the paper has not been subjected to Agency review and no official endorsement should be inferred.

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